# REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188



| 1. REPORT DATE *(DD-MM-YYYY)* | 2. REPORT TYPE | 3. DATES COVERED *(From - To)* |
|---|---|---|
| | Technical Papers | |

**4. TITLE AND SUBTITLE**

Please see attached

**5a. CONTRACT NUMBER**

**5b. GRANT NUMBER**

**5c. PROGRAM ELEMENT NUMBER**

**6. AUTHOR(S)**

**5d. PROJECT NUMBER**
2302

**5e. TASK NUMBER**
M1G2

**5f. WORK UNIT NUMBER**
346120

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

Air Force Research Laboratory (AFMC)
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**8. PERFORMING ORGANIZATION REPORT**

**9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

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**10. SPONSOR/MONITOR'S ACRONYM(S)**

**11. SPONSOR/MONITOR'S NUMBER(S)**
Please see attached

**12. DISTRIBUTION / AVAILABILITY STATEMENT**

Approved for public release; distribution unlimited.

**13. SUPPLEMENTARY NOTES**

**14. ABSTRACT**

20030127 213

**15. SUBJECT TERMS**

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| a. REPORT | b. ABSTRACT | c. THIS PAGE | A | | Leilani Richardson |
| Unclassified | Unclassified | Unclassified | | | 19b. TELEPHONE NUMBER *(include area code)* (661) 275-5015 |

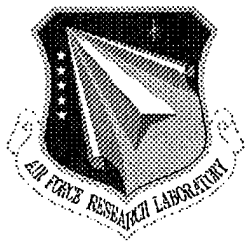
TP-FY99-0108

2302M1G2 ✓ Spreadsheet ✓ DTS

MEMORANDUM FOR PRR (In-House Publication)

FROM: PROI (TI) (STINFO) 24 May 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-FY99-0108
Gordon, Voth, Pachter, Boatz, "DoD High Performance Computing Challenge Project: New Materials Design"
**Presentation** **(Public Release)**




# DoD High Performance Computing Challenge Project

## New Materials Design

**Prof. Mark S. Gordon, Iowa State University**

**Prof. Gregory Voth, University of Utah**

**Dr. Ruth Pachter, AFRL/MLPJ**

**Dr. Jerry Boatz, AFRL/PRS**

DoD HPC Users Group Conference

Monterey, CA

7-11 June 1999


# New Materials Design

## OUTLINE

**1. Project Overview**

**- Atom-doped solid hydrogen and high energy density molecules as advanced rocket propellants**

**- "Explosive" annulenes as possible route to new nanostructural materials**

**2. Theoretical Methods, benchmarks**

**- Centroid Molecular Dynamics**

**- Ab initio electronic structure theory**

**3. Results**

**4. Future Directions**

# New Materials Design

## OVERVIEW

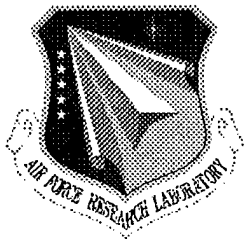
1. Propellants

- Solid hydrogen doped with high energy species (e.g., atoms) offer revolutionary improvements in rocket propulsion over currently used $LOX/LH_2$ (SSME).

- High energy density molecules may improve performance of traditional solid and liquid propellants.

2. "Explosive" annulenes

- Precursors to carbon nanotubes, may provide route to heteroatomic nanostructural materials.

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## COMPUTATIONAL METHODS

1. **Centroid Molecular Dynamics (CMD*)**

   **- Simulation method developed by Prof. Voth which properly treats quantum effects (e.g., zero point vibrational energy, tunneling). Essential for reliable characterization of solid hydrogen (low temperatures, light particles.)**

2. **Ab Initio Electronic Structure Theory (GAMESS*, G94, ACESII,...)**

   **- Approximate solutions of Schrodinger equation applied to molecules. Prediction of molecular structures, energies, reaction pathways and stabilities, synthetic routes, spectroscopic constants, solvation effects, etc.**

* CHSSI codes

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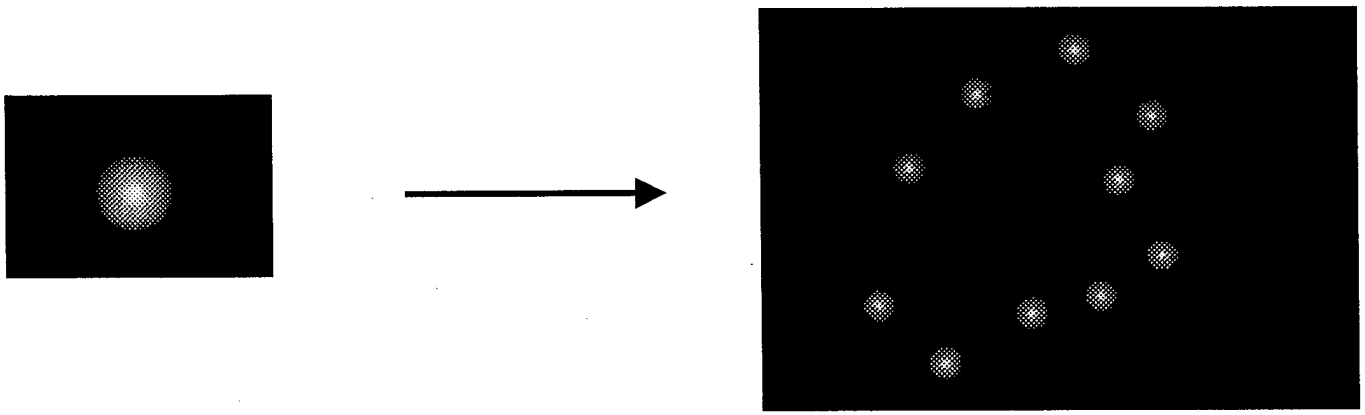
## CENTROID MOLECULAR DYNAMICS

**Simulation method based on path integral techniques for mapping quantum particles onto "polymer ring" of classical quasiparticles:**



**Each "real" particle is replaced by N ( 50<N<500) quasiparticles; classical dyanmics done on collection of quasiparticles => natural, efficient parallelism.**

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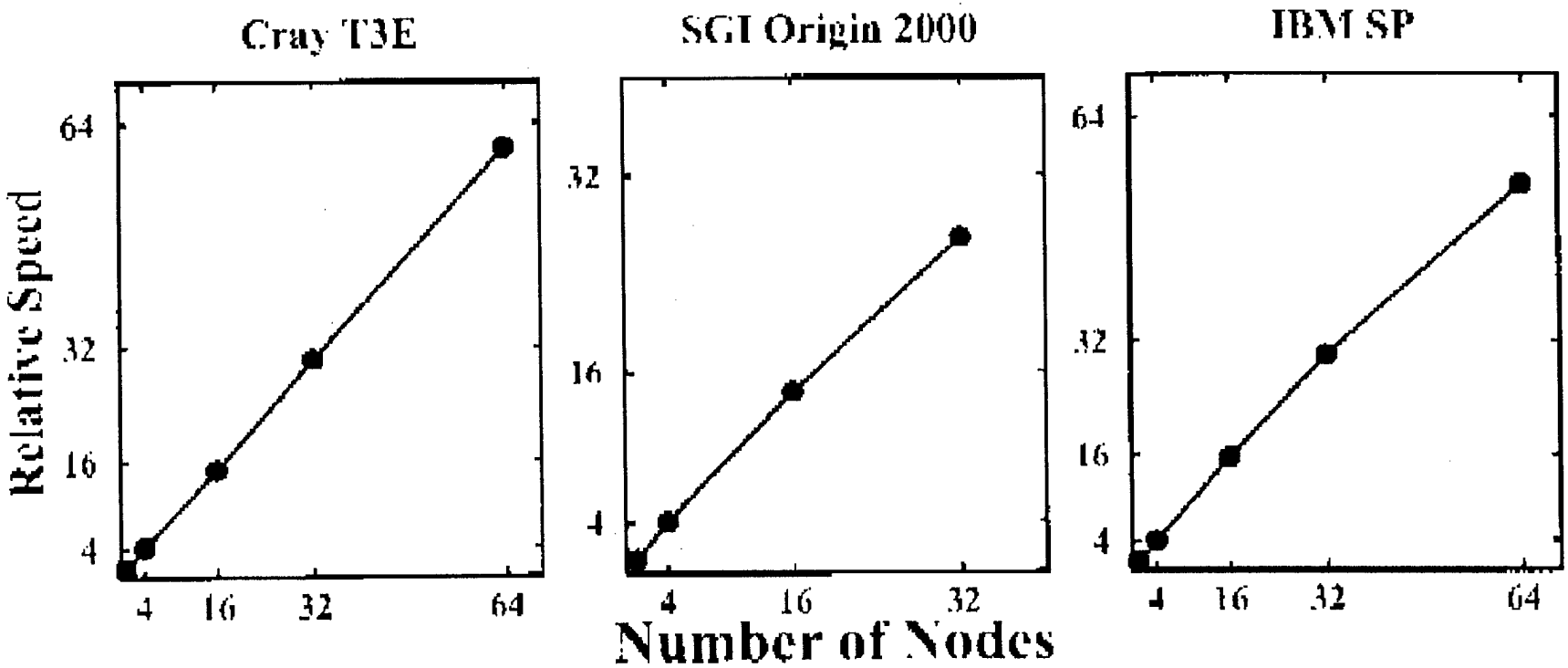
Centroid Molecular Dynamics code shows linear scaling!

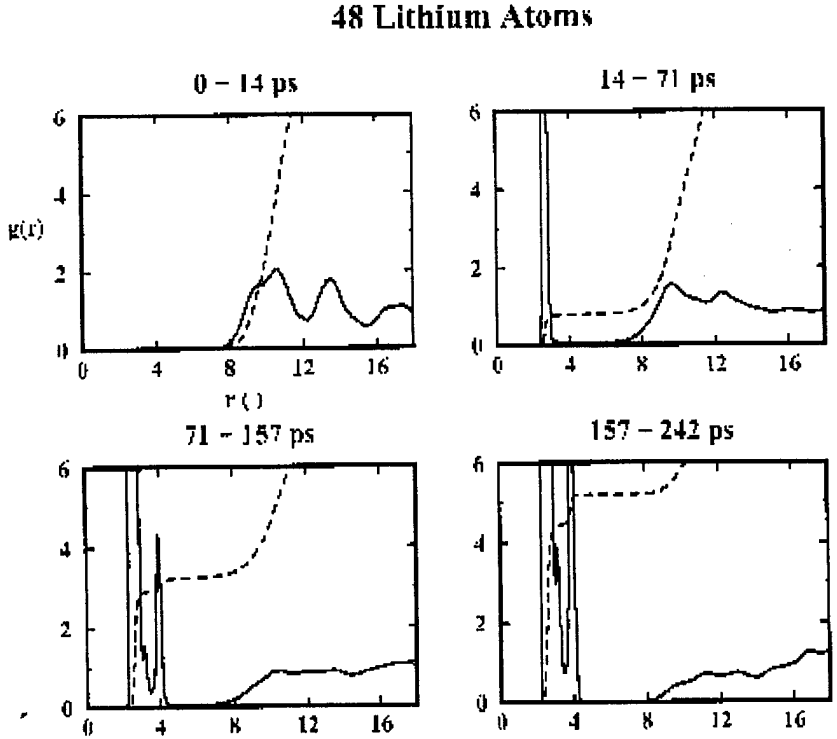


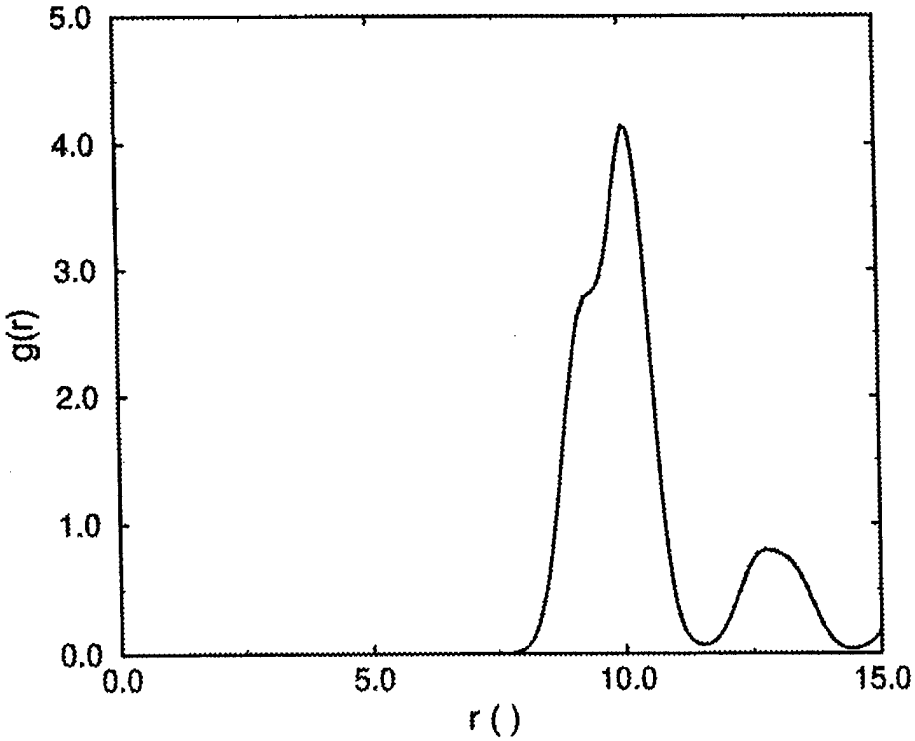
# New Materials Design

3.3 % lithium atoms in solid $H_2$ are stable for only 10 picoseconds

6 % boron atoms in solid $H_2$ are stable for nanoseconds

Computational requirements: 6 ps trajectory of 400-atom system takes 10,000 node-hours on 120Mhz SP

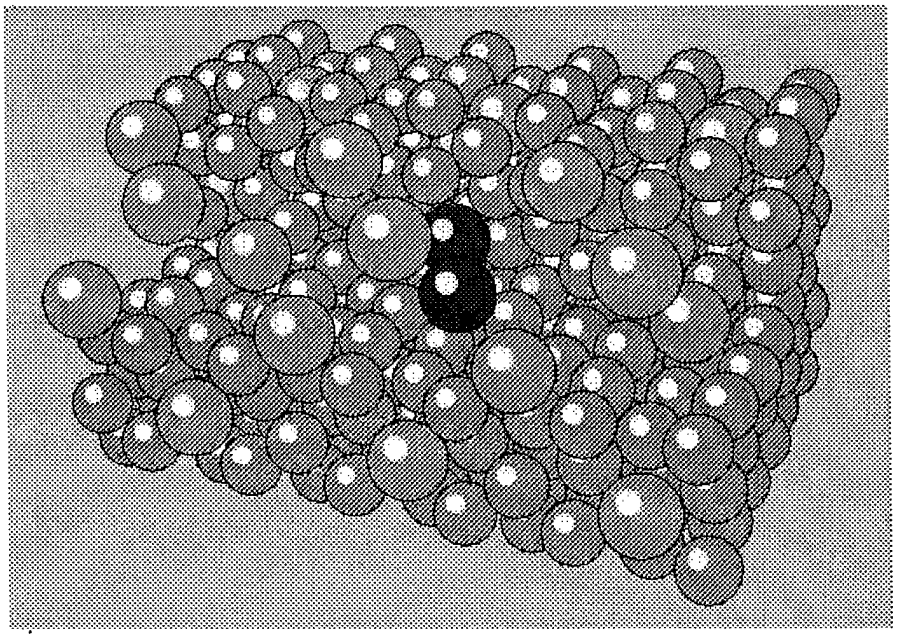


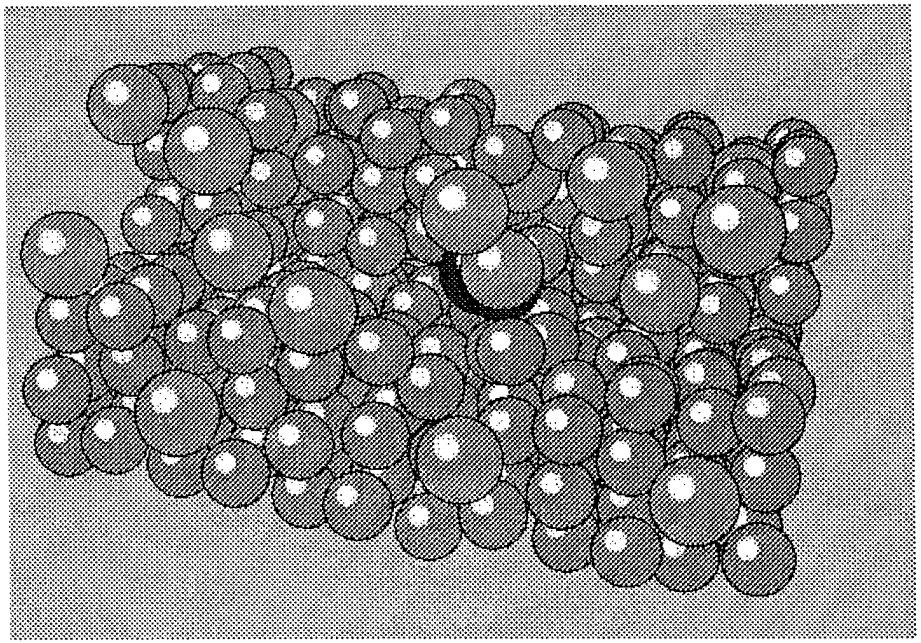
# New Materials Design

## 6.25% boron atoms in solid *para*-hydrogen

Before reaction. Reacting boron atoms are shown in red. (Some hydrogens are hidden for viewing convenience.)



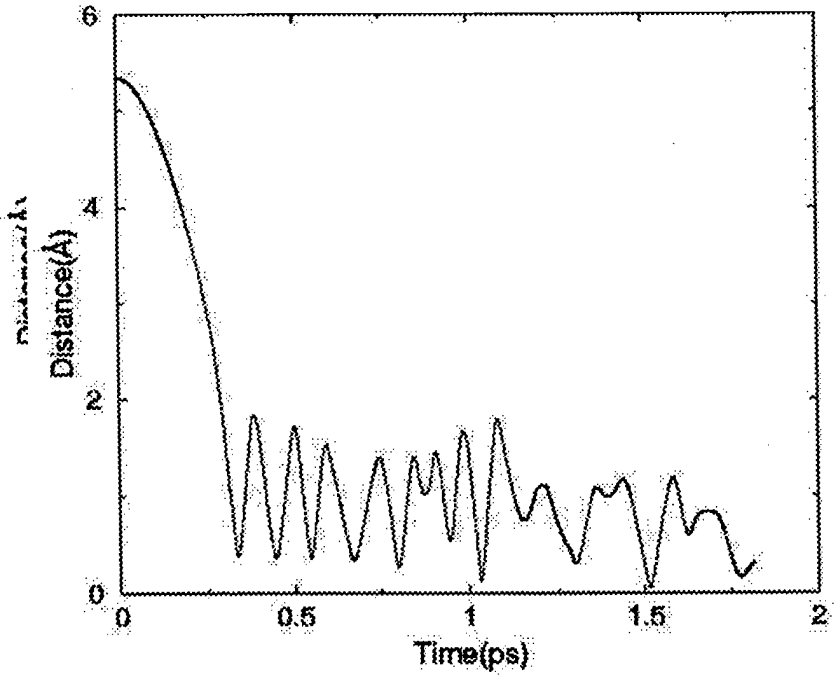
After reaction. (Note only local recombination of impurities! )



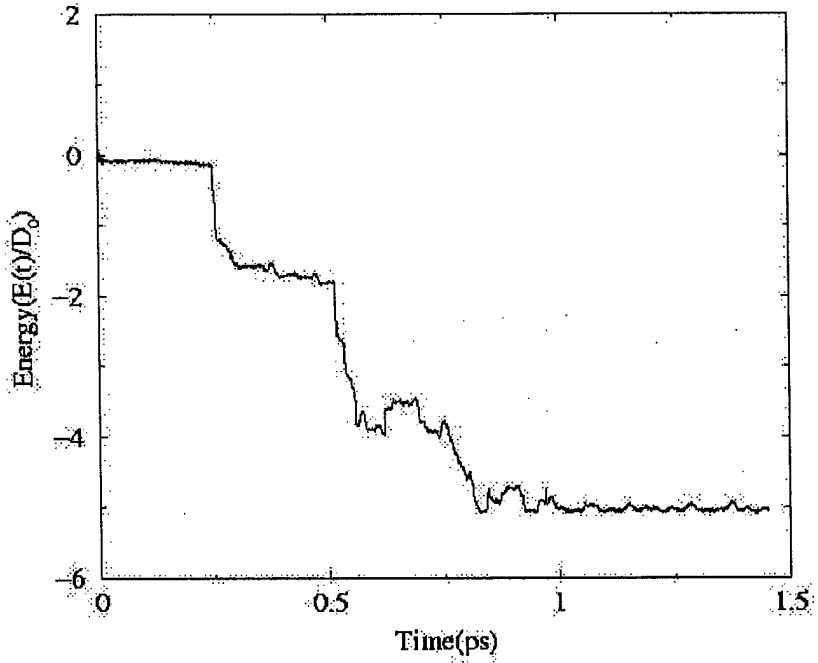
# New Materials Design

## 6.25% boron atoms in solid *para*-hydrogen

Distance between two tagged boron atoms as a function of time.




Released energy as a function of time for the same system. $D_0$ is the boron-boron interaction well depth.



# New Materials Design

## Computational Approach in Electronic Structure Theory

**Attempt to solve the time-independent Schrodinger equation for a molecule**

$$H\,\Psi(r_e;R_N) = E\,\Psi(r_e;R_N)$$

**H = quantum mechanical Hamiltonian operator**

$$= -\sum_i 1/2\,\nabla^2_i - \sum_N 1/2M_N\,\nabla^2_N - \sum_i \sum_N Z_N/R_{iN} +$$
$$\sum_i \sum_{j>i} 1/R_{ij} + \sum_M \sum_{N>M} Z_M Z_N/R_{MN}$$

**E = total energy of the molecule**

$$\Psi(r_e;R_N) = \text{molecular wavefunction}$$


# New Materials Design

## Current Status of parallel GAMESS

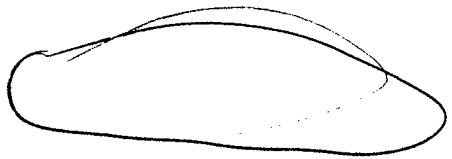
| | RHF | ROHF | UHF | GVB | MCSCF |
|---|---|---|---|---|---|
| Energy | cdp | cdp | cdp | cdp | cdp |
| Analytic Gradient | cdp | cdp | cdp | cdp | cdp |
| Numeric Hessian | cdp | cdp | cdp | cdp | cdp |
| Analytic Hessian | cdp | cdp | - | cdp | - |
| MP2 energy | cdp | cdP | cdP | - | c |
| MP2 gradient | cdP | - | - | - | - |
| CI energy | cdp | cdp | - | cdp | cdp |
| CI gradient | cd | - | - | - | - |

c = conventional disk storage of AO integrals

d= direct evaluation of AO integrals

p = parallel exection

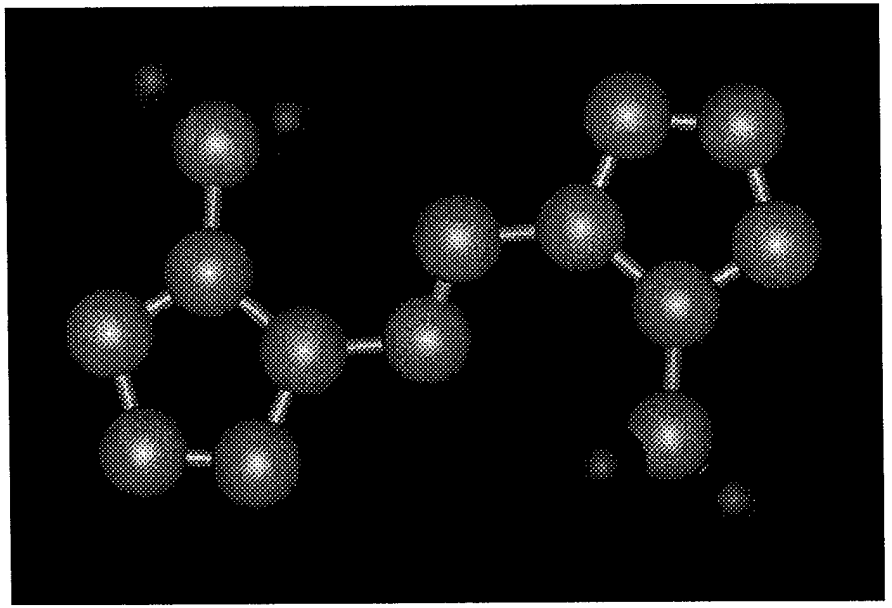
P =



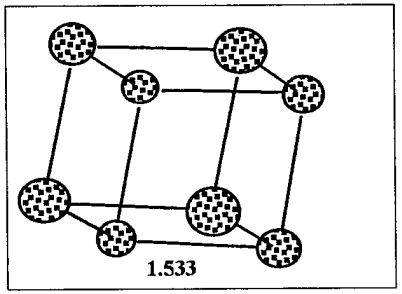
# New Materials Design

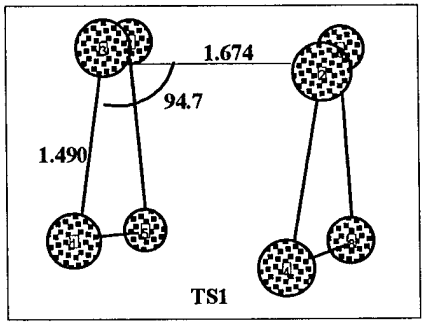
**Calculated heat of formation (energy content relative to elements in their standard states) = 457 kcal/mol. Specific impulse ($I_{sp}$) = 329 sec.**

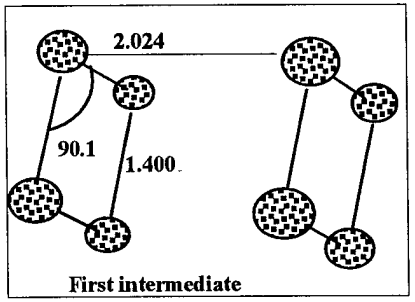
**$I_{sp}$ of hydrazine = 240 seconds, $I_{sp}$ of RP-1/LOX = 300 sec.**

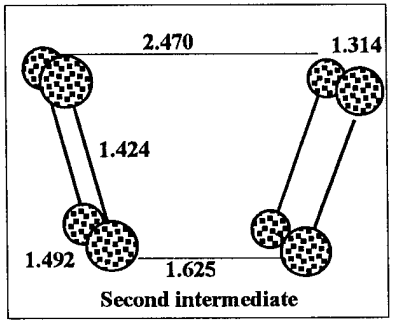


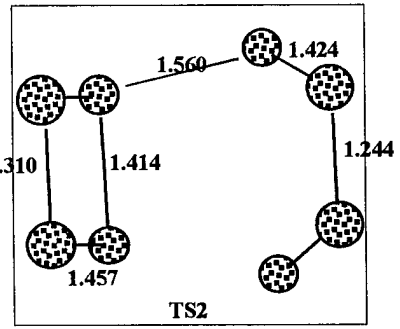
# New Materials Design

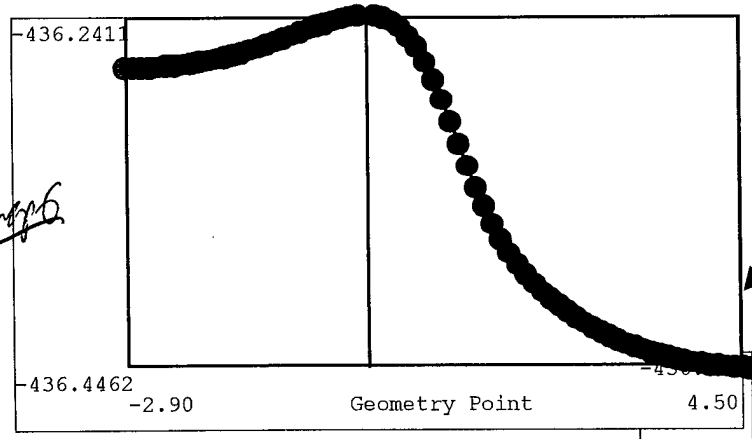


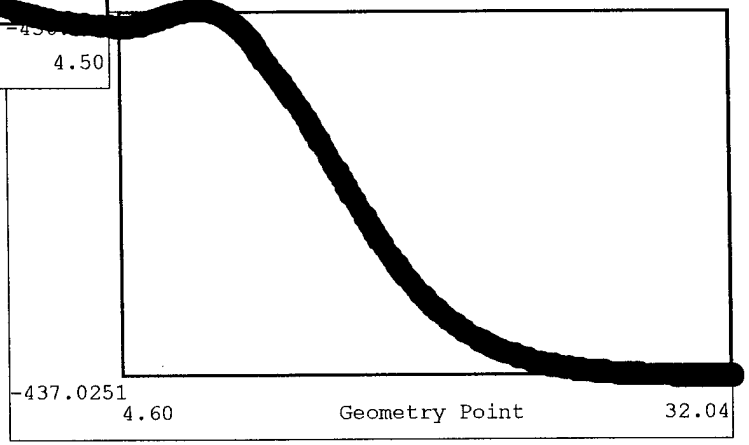



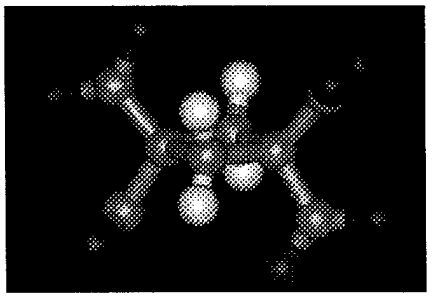



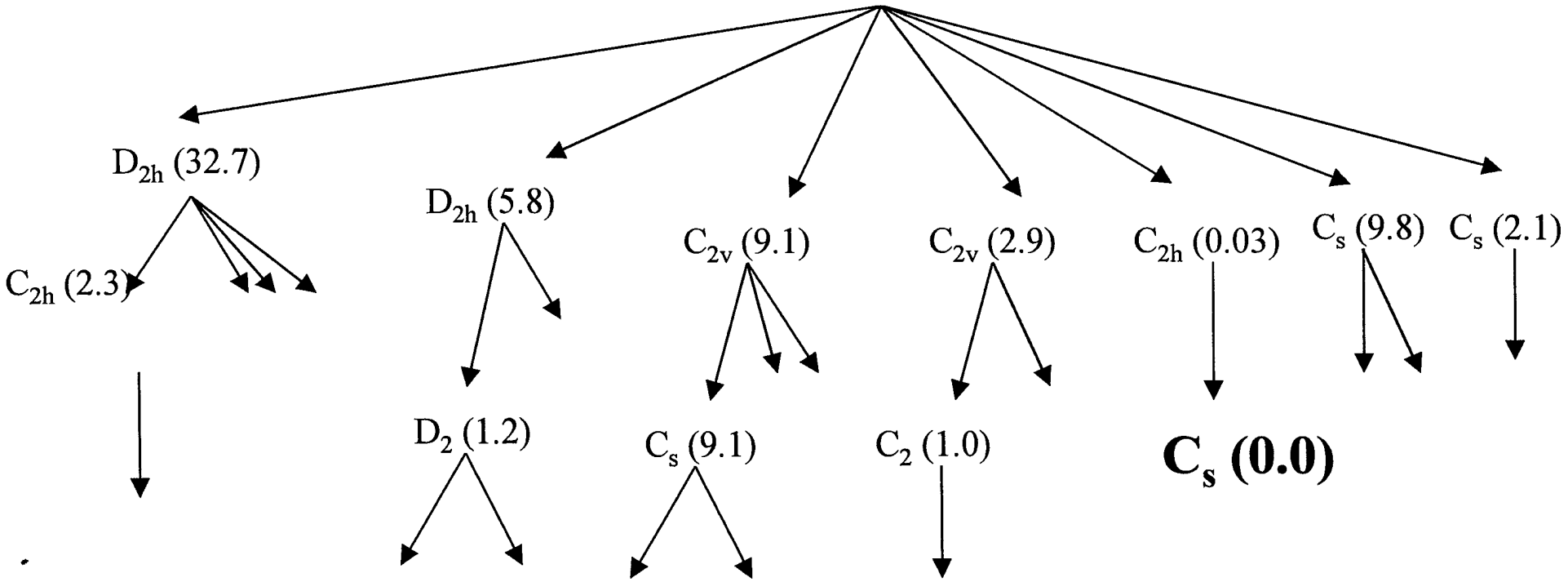




$4N_2$
-473 kcal

# New Materials Design

**Potential Energy Surfaces can be very complicated**

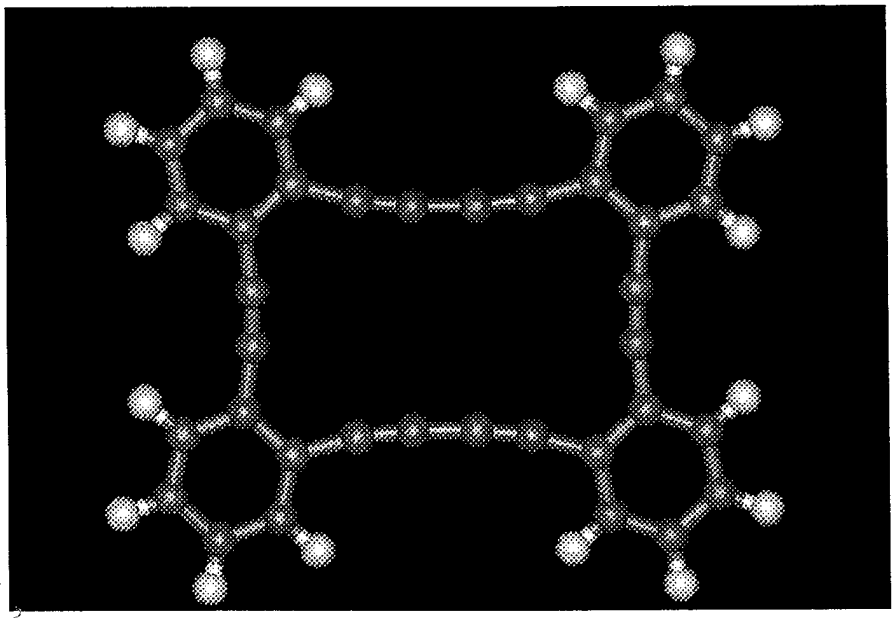


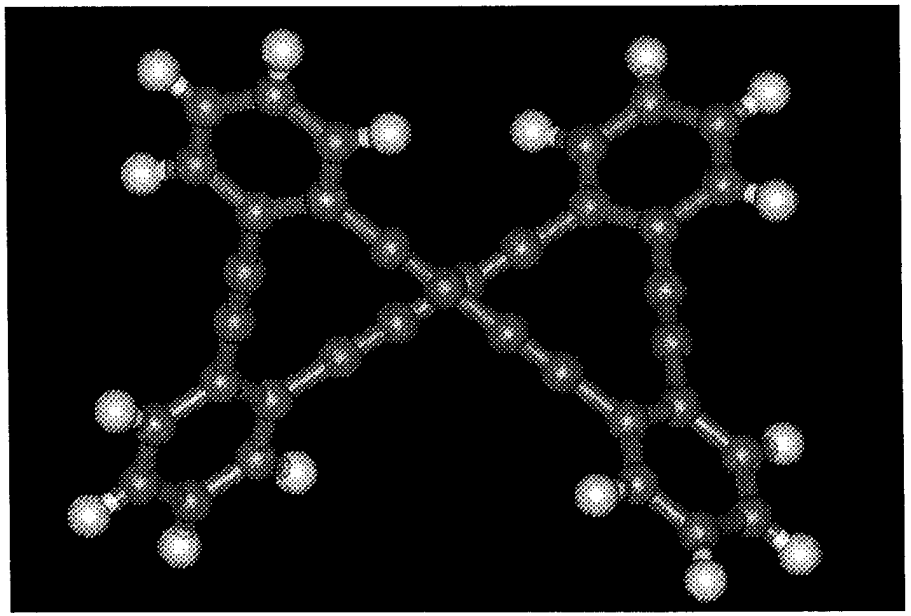


# New Materials Design

## "Explosive" Annulenes

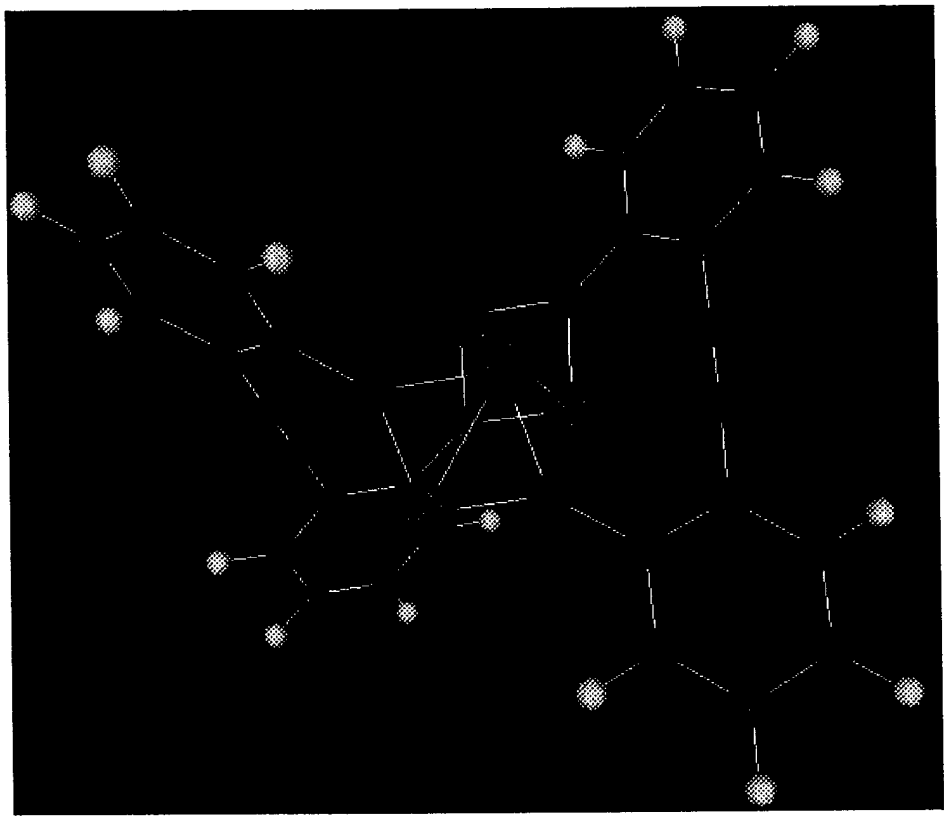
## Decompose at 245° C, products include carbon nanotubes and "onion" fullerenes!





# New Materials Design

## "Explosive" Annulenes: silicon derivatives: possible route to heterofullerenes??



Computational requirements:

Geometry optimization plus numerical hessian: 10,000 node hours/conformation

MP2 energies: 1.8 GW on 20 IBM SP nodes.

# New Materials Design

## CONCLUSIONS

1. In solid hydrogen, boron atoms are more stable than lithium atoms.
2. $C_2N_{12}O_4$ is superior to hydrazine and RP-1/LOX. Unresolved issues: kinetic stability, environmental interactions.
3. $N_8$ is probably too unstable for propulsion applications.
4. CHSSI has had a positive impact on CCM !!


# New Materials Design


## ACKNOWLEDGEMENTS

**Iowa State University**

**Dr. Galina Chaban**
**Dr. Graham Fletcher**
**Prof. Takako Kudo**
**Ms. Vassiliki-Alexandra Glezakou**

**University of Utah**

**August Calhoun**
**Marc Pavese**
**Dan Berard**
**Soonmin Jang**

**Air Force Research Laboratory**

**Dr. Jeffrey D. Mills**
**Dr. Jeffrey A. Sheehy**
**Dr. Hi Young Yoo**

**Aeronautical Systems Center**

**Dave Semeraro (PET)**

MHPCC

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